TESTING OF THE SYNCHRONOUS FLUORESCENCE IN APPLICATION TO USED LUBRICATE OIL CHARACTERISATION

Emilia Baszanowska, Zbigniew Otremba

Gdynia Maritime University
Faculty of Marine Engineering, Department of Physics
Morska Street 81-87, 81-225 Gdynia, Poland
tel.: +48 58 6901504, fax: +48 58 6206701
e-mail: eba@am.gdynia.pl, zotremba@am.gdynia.pl

Abstract

Reliability of the ship propulsion system depends, inter alia, on the quality of lubricate oils. Research indicates that exploitive features of oil are reduced with it runtime in the ship engine circuit. At the present the basic parameters representing exploitive features of oil are: water content, total acid number and total base number or viscosity vs. temperature, anti-wear performance, further: content of additives and their concentrations, reaction products, and other contaminating substances, also magnetically separated large ferromagnetic particles, the size, the shape, the composition and concentration of the abnormal wear particles. Additional properties of oil are described based on atomic emission spectroscopy, granulometry of separated from the lubricant sample by magnets and gravity, permeability changes, as well as rheometric and tribometric characteristics. Complexity of composition of lubricate oil raises the idea to use changes of relative content of any compounds for characterization of oil exploitive features. Fluorescence method is possible to use for oil properties characterisation due to the presence mono and polycyclic compounds in oil that induces fluorescence phenomenon. Therefore identification the fluorescence spectra when exploitation time of oil increases could be novel indicator to monitor of lubricate oil exploitive quality. In this study we present changes of oil fluorescence expressed by synchronous spectra, taking into account working time of exemplary lubricate oil in the ship engine.

Keywords: marine fleet exploitation, lubricate oil, fluorescence spectroscopy, synchronous fluorescence spectra

1. Introduction

Intensive and permanently evolved land and maritime transport forced necessity to improve economical efficiency as well as human and environmental safety. If the sea areas are considered, significant role in the safe and more convenient maritime transport plays the smooth and safety operation of all devices in the whole ship technical system.

The functioning efficiency of the ship engine strongly depends of the quality of lubricate oils. The quality of oil is lost with runtime in engine ship and in consequence, the exploited oil properties are gradually reduced. Therefore, a need easy monitor the quality of exploited oil in the motor engine grows. The properties of oil are expressed by several indicators. The basic parameters characterizing exploited oil are: water content, total acid number and total base number or viscosity vs. temperature [1], anti-wear performance as well as content of enriching additives, reaction products, and other unfavourable contaminations [5, 11], magnetically separated large ferromagnetic particles, the size, the shape, and concentration of the abnormal wear particles [10]. Additional properties of oil are described based on atomic emission spectroscopy, granulometry of separated from the lubricant sample by magnets and gravity, permeability changes [12]. Additionally for oil, signatures belong also rheometric and tribometric characteristics [8, 13].

The highly complex composition of lubricate oil (mainly hydrocarbons) [6] raises the idea to use changes of relative content of define compounds for characterization of oil exploitive features. Fluorescence method is possible to use for oil properties characterisation due to the presence mono and polycyclic compounds that induces phenomenon of oil fluorescence [7]. The fluorescence

spectroscopy is commonly used to protect the natural marine environment by the identification or detection of oil pollution [2-4, 9]. Therefore, changes of intensity of oil fluorescence, identified for define excitation wavelength in define emission wavelength, reflects changes taking place in composition of oil during its exploitation.

In this study we present changes of oil fluorescence expressed by synchronous spectra, taking into account working time of exemplary lubricate oil in the ship engine.

2. Material and method

Lubricate oil *Titan Truck Plus 15W40* (*TTP 15W40*) in four forms, respectively, fresh oil and used oil exploited 178 hours, 342 hours and 1024 hours in engine *3AL 25/30 Cegielski-Sulzer* (with the power 396 kW, was applied). Photographic views of samples of oils, observed in visual (VIS) and ultraviolet (UV) light in Fig. 1 are shown. Every sample of oil is visible in UV (blue light) – this phenomenon was one of motivation to apply spectrofluorometer with excitation wavelengths from UV range. These oils were individually dissolved in n-hexane. The measurement were performed basing on the concentration of oil is the solvent equal to 100 mg/kg. Excitation-emission (EEM) spectra of oil samples were measured using spectrofluorometer *Hitachi F-7000 FL*. Quartz cuvette of dimensions 1×1 cm were applied.

The following measurement parameters were applied: excitation wavelength from 200 nm to 340 nm with excitation sampling interval 5 nm, emission wavelength from 260 nm to 450 nm with emission sampling interval 5 nm, excitation slit 5 nm; emission slit 5 nm, integration time 0.5 s and photomultiplier tube voltage 400 V. At the beginning, EEM spectra for n-hexane solvent at a stabilised temperature 20°C were performed. Next, spectra of oil diluted in n-hexane for particular four oil samples were performed. Finally, to obtain the real spectra of lubricate oil each date of measured oil samples diluted in n-hexane were corrected by subtraction the spectra of pure n-hexane.
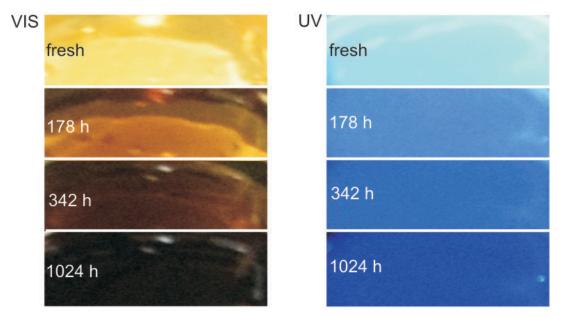

Fig. 1. View of oil samples in visual light (left) and in ultraviolet (right)

3. Results

Figure 2 presents results of measurements of excitation-emissions spectra for two exemplary oils (fresh and exploited 1024 hours in the engine circuit). Straight diagonal lines represent cross-sections resulting in synchronous spectra for various offsets (60, 80 and 100 nm).
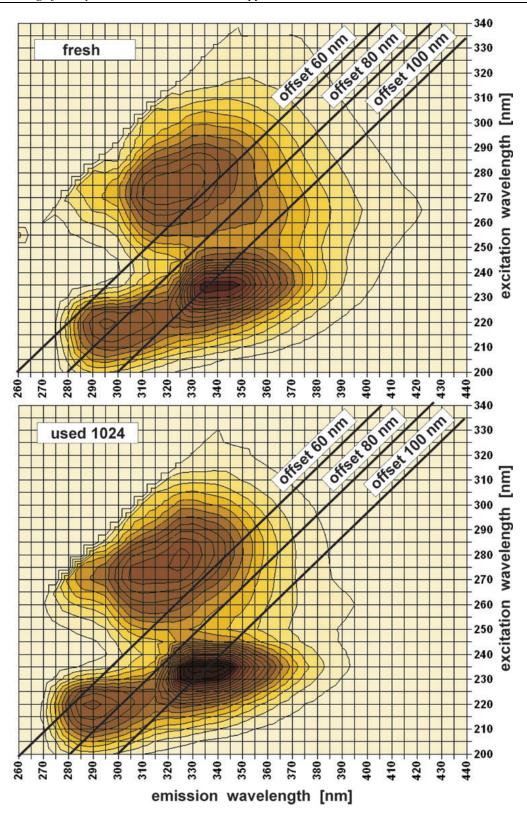
Fig. 2. Excitation-Emission Fluorescence spectra of two used oils: fresh and used one (1224 hours in the engine circuit). Straight diagonal lines show cross-sections resulting in the creation of synchronous fluorescence spectra plotted in Fig. 3

Based on measured EEM spectra of oils, synchronous spectra were determined for three values of wavelength interval ($\Delta\lambda$) – so-called offset (which is permanent difference between excitation and emission wavelengths): 60, 80 and 100 nm. Obtained synchronous fluorescence spectra are exposed as graphs in Fig. 3 separately for three applied offsets.
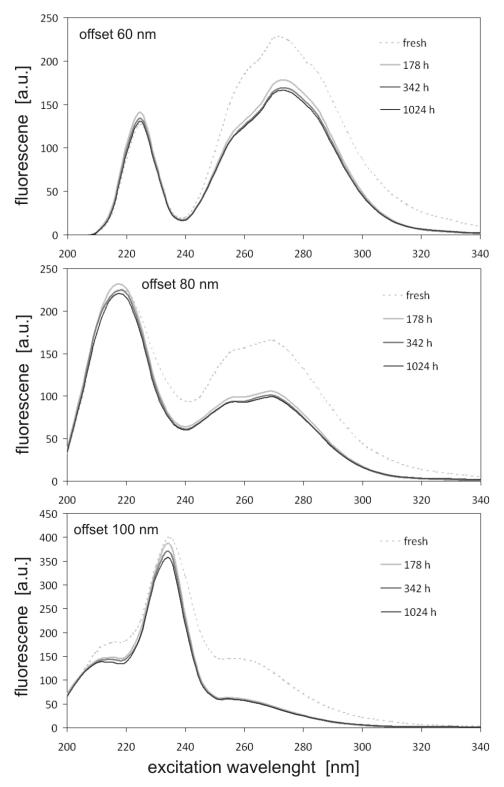
Fig. 3. Fluorescence spectra of oils for constant wavelength internal 60 nm, 80 nm and 100 nm (distance between excitation and emission wavelengths)

For offset 60 nm two maxima are shaped, namely for excitation around 230 nm (lower) and 270 nm (greater). Similarly for offset 80 nm, but in this case for 230 nm peak is greater than for 270 nm. For offset 235 nm, one high peak exists. The courses of plots for fresh oil are higher than for used oils (the longer the time of work in engine, the graph runs lower).

The strongest changes in the shape of synchronous spectra are placed in the initial phase of working in the engine circuit. Differences between spectra are slight for times longest than 178 h.

4. Discussion

Results presented above demonstrate strong changes of intensity of fluorescence with parallel changes of excitation and emission wavelength. However, the character of those changes depends on distance between wavelengths of excitation and emission (offset). For offset 60 nm four distinct peaks, one can identify whereas for offsets 80 and 100 nm rather only three ones are clearly visible. Taking into account an exemplary spectrum an attempt was made to identify a series of Gaussian curves which, by addition, make up the define spectrum course. In Fig. 4 there is shown spectrum for exemplary used oil (178 h) as the sum of Gaussian curves. Analysing such inverse problem we conclude that there exists at least seven peaks for offset equal 60 nm. Each peak can be assigned to a specific chemical compound, most likely polycyclic aromatic hydrocarbons (PAHs). Possible to assign the identified peaks to specific chemicals would require additional complicated instrumental analysis like chromatography and mass spectroscopy.
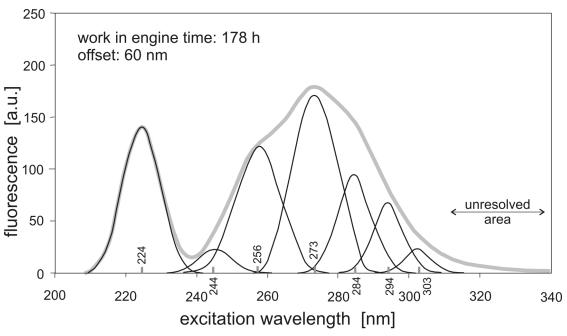

Fig. 4. Exemplary synchronous spectrum been divided into Gaussian curves

In next studies it is worth to check whether configuration of positions and altitudes of peaks may play, a role of indicator of degradation degree of lubricates oil in engine circuit. Taking into account above presented synchronous spectra of oils for different explanation time in ship engine one can conclude that the synchronous fluorescence would be useful for first several hundred hours of work of oil.

5. Conclusions

In the study synchronous fluorescence spectroscopy was used to characterize the properties of lubricate oil with exploitation time in engine system. To describe the changes of oil synchronous florescence spectrum with runtime in the ship engine the distribution of spectrum on the several Gaussian curves was applied. Obtained initial results indicate several peaks, which can be assigned to several polycyclic aromatic hydrocarbons - PAHs, which can be the indicators for oil exploited in engine system. Values of offsets applied in this paper are exemplary and on the present stage of investigations not fixed. At all events synchronous spectrum is made up of much smaller amounts of data and requires much less time to measure than EEMs. That approach seems to be a likely tool for exploited oil characterisation.

Acknowledgements

References

[1] Agoston, A., Ötsch, C., Jakoby, J., *Viscosity sensors for engine oil condition monitoring-Application and interpretation of results*, Sensors and Actuators A: Physical, Vol. 121, No. 2, pp. 327-332, 2005.

[2] Baszanowska, E., Zielinski, O., Otremba, Z., Toczek, H., *Influence of oil-in-water emulsions on fluorescence properties as observed by excitation-emission spectra*, J. Europ. Opt. Soc. Rap. Public., Vol. 8, No. 13069, pp. 13069-1 - 13069-5, 2013.

[3] Baszanowska, E., Otremba, Z., *Oil identification based on total synchronous spectra*, Journal of KONES Powertrain and Transport, Vol. 21, No. 2, pp. 15-20, Warsaw 2014.

[4] Baszanowska, E., Otremba, Z., Toczek, H., Rohde, P., *Fluorescence spectra of oil after it contacts with aquatic environment*, Journal of KONES Powertrain and Transport, Vol. 20, No. 3, pp. 29-34, Warsaw 2013.

[5] Borin, A., Ronei, J., Poppi, R. J., *Application of mid infrared spectroscopy and iPLS for the quantification of contaminants in lubricating oil*, Vibrational Spectroscopy, Vol. 37, No. 1, pp. 27-32, 2005.

[6] Geddes, C.D., Lakowicz, J.R, *Review in fluorescence* 2005, Springer 2005.

[7] Mathew, M., *A comparison study of gravimetric and ultraviolet fluorescence methods for the analysis of total petroleum hydrocarbons in surface water*, Civil Engineering Master's Theses, Paper 1, 2009, http://hdl.handle.net/2047/d10019236 [Online] 2016-05-30.

[8] Młynarczak, A., *Investigation of the influence of aftermarket additive on lubricating properties of Titan Truck Plus 15W40 oil used in marine diesel engines*, Zeszyty Naukowe Akademii Morskiej w Gdyni, No. 76, pp. 62-68, 2012 (in Polish).

[9] Otremba, Z., Targowski, W., Toczek, H., *Fluorescence as a scanning method for oil type identification in the sea environment*, 3rd Safety and Reliability International Conference KONBiN'03, 2003.

[10] Seifert, W.W., Westcott, V. C., *A method for the study of wear particles in lubricating oil,* Wear, pp. 27-42, 1972.

[11] Stuart, A.D., Trotman, S.M., Doolan, K.J., Fredericks, P.M., *Spectroscopic Measurement of Used Lubricating Oil Quality, Applied Spectroscopy*, Vol. 43, No. 1, pp. 55-60, 1989.

[12] Voelker, P.J., Hedges J.D., *Oil quality sensor measuring bead volume*, Patent US5777210A, 1998.

[13] Wierzcholski, K., Miszczak, A., *Algorythm for variable pseudoviscosity coefficients under experimental basis*, Tribologia, Vol. 44, No. 4, pp.125-136, 2013.